

A STUDY OF GROUND WATER SAMPLED FROM SELECTED AREAS
IN CALIFORNIA IN 1981 FOR CIS- AND TRANS-CHLOROALLYL
ALCOHOLS, THE PRIMARY DEGRADATION PRODUCTS OF
1,3-DICHLOROPROPENE (TELONE II)

by

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SUMMARY

Concerns have been raised that cis- and trans-chloroallyl alcohols, the primary degradation products of 1,3-dichloropropene found in the pesticides Telone II and DD, might persist in soil to which Telone II or DD had been applied, and then migrate into groundwater sources. A study of water from 54 wells in California which were sampled in January 1981 for residues of 1,3-dichloropropene found no detectable residues of that compound. Follow-up water samples were collected from 8 of these same wells in Fresno and Merced Counties in June 1981, and were analyzed for cis- and trans-chloroallyl alcohols. No residues were found at a sensitivity level of 0.6 ppb. The half-life of chloroallyl alcohol in water is approximately 7 days.

INTRODUCTION

The circumstances leading to the suspension of DBCP have heightened concerns over groundwater intrusion of soil-applied fumigants and their breakdown products. Telone II (cis- and trans-1,3-dichloropropene) is a preplant nematocidal fumigant used on numerous orchard and row crops in California. In early 1981, the Department of Food and Agriculture conducted studies monitoring the presence of Telone II in groundwater supplies in the San Joaquin Valley. Fifty-four wells located in Telone high-use areas were sampled. Analysis of these samples revealed no detectable residues of either isomer of 1,3-dichloropropene down to a sensitivity of 0.1 ppb. Concerns were raised within the Water Resources Control Board (WRCB) that cis- and trans-chloroallyl alcohols, primary degradation products of Telone II, were persistent enough to become groundwater contaminants. Baines, et al (1977) reported that high concentrations of 1,3-dichloropropene (62.4-250 ppm) interfered with microbial degradation of chloroallyl alcohol.

Although toxicity data is nearly nonexistent on chloroallyl alcohols, they possess the chloroallyl moiety which is common to a number of mutagenic compounds (i.e., the herbicide Vegedex, 2-chloroallyl-diethyldithiocarbamate, now being removed from the market). These concerns over the potential hazards of chloroallyl alcohols were enough for the WRCB to request a groundwater monitoring study for the compounds. This study was conducted by the Department of Food and Agriculture because the WRCB did not possess adequate field staff and analytical facilities.

MATERIALS AND METHODS

Municipal groundwater supplies were sampled in the communities of Ripon, Manteca, Firebaugh, San Joaquin, Tranquility, Atwater, and Livingston, areas previously identified as Telone high-use areas (Maddy, et al, 1981). Water samples were collected in accordance with the methods used in previous groundwater monitoring projects conducted by CDFA's Worker Health and Safety Unit (Peoples, et al, 1980; Maddy, et al, 1981). Analysis was performed within 24 hours of sampling.

Cis- and trans-chloroallyl alcohols were extracted from water by partitioning with diethyl ether. The ether extract was evaporated to near dryness and the residue was redissolved in hexane. The hexane extract was made up to a final volume before analysis by gas-liquid chromatography. Recoveries were nearly 100 percent. Analysis was performed on a Varian 3700 Chromatograph equipped with a Tracor Hall 700A Conductivity Detector. Chromatographic conditions are as follows: 6 ft. x 2 mm (i.d.) glass column packed with 10 percent SP2100 on 100/120 chromosorb WHP. Flow rates: 25ml/min. helium (column) and 35 ml/min. hydrogen (reaction chamber gas). Temperatures: injector - 150°C., column - 135°C., reactor - 810°C. Solvent flow rate: 0.3-0.5 ml/min., isopropanol.

An in-laboratory breakdown study of chloroallyl alcohol in water was conducted. A liter of uncontaminated well water was spiked with 65 ppb of a mixed isomer standard, capped with foil and screw cap, and left out in the laboratory at room temperature. Samples were collected periodically and analyzed with the analytical protocol.

RESULTS

No detectable residues of cis- or trans-chloroallyl alcohols were detected in the 8 groundwater samples collected. The minimum detectable level of the analysis was 0.6 ppb. Depths of the wells sampled ranged from 200 to 600 feet.

The results of the in-laboratory degradation study were as follows:

<u>Time (hours)</u>	<u>Chloroallyl alcohol residue in water (sum of the mixed isomers) (ppb)</u>
0	62
1	57
24	50
48	51
72	51
96	49
168	39

The half-life of chloroallyl alcohols in water appears to be approximately 7 days.

DISCUSSION

Cis- and trans-1,3-dichloropropene (1,3-D) reportedly has a soil half-life of approximately 4 weeks as revealed by laboratory studies (Roberts and Stoydin, 1976). 1,3-D is readily hydrolyzed, in moist soils, to cis- and trans-chloroallyl alcohols (Castro and Belser, 1966). 1,3-D disappears in sandy soils at 15-20°C. (closed containers) at a rate of 2-3.5% a day. In clay-containing soils, this rate could be as much as 25% a day (Van Dijk, 1974). Degradation is influenced heavily by soil moisture content, clay content, and temperature (McHenry and Thomason, 1974).

Chloroallyl alcohols disappear (in sandy soils at 15°C.) 4.5 times as fast as the parent dichloropropenes for the cis-isomer, and 6.5-12 times as fast for the trans-isomer. The half-lives are on the order of 1 day for the cis-isomer and 2 days for the trans-isomer (Van Dijk, 1974). Degradation of chloroallyl alcohols is reported to occur by microbial dehalogenation (Belser and Castro, 1971). Chloroallyl alcohols are reported to be strongly bound to soil components (Roberts and Stoydin, 1976).

CONCLUSIONS

Residues of cis- and trans-chloroallyl alcohols were not detected in municipal groundwater supplies in areas of the San Joaquin Valley where the parent compounds cis- and trans-1,3-dichloropropene (Telone II) have been used as a nematocide for over 20 years. In laboratory studies, the half-life of a mixture of cis- and trans-chloroallyl alcohols in water was estimated to be 7 days.

REFERENCES

- Baines, R. C.; L. J. Klotz, and T. A. DeWolfe. Some biocidal properties of 1,3-D and its degradation product. Phytopathol. 67:936-940 (1977).
- Belser, N. O. and C. E. Castro. Biodehalogenation - the metabolism of the nematocides cis- and trans-chloroallyl alcohol by a bacterium isolated from soil. J. Agr. Food Chem. 19:23-26 (1971).
- Castro, C. E. and N. O. Belser. Hydrolysis of cis- and trans-1,3-dichloropropene in wet soil. J. Agr. Food Chem. 14:69-70 (1966).
- Maddy, K. T., et al. A study of well water in selected California counties for detecting pesticide residues of 1,3-dichloropropene, 27 organophosphates, and 23 chlorinated hydrocarbons. California Department of Food and Agriculture Report HS-854 (1981).
- McKenry, M. V. and I. J. Thomason. 1,3-dichloropropene and 1,2-dibromoethane compounds: I. Movement and fate as affected by various conditions in several soils. Hilgardia. 42:393-421 (1974).
- Peoples, S. A., et al. A study of well water collected from selected areas in California to determine the presence of DBCP and certain other pesticide residues. Bull. Environ. Contam. Toxicol. 24:611-618 (1980).
- Roberts, T. R. and G. Stoydin. The degradation of (Z)- and (E)-1,3-dichloropropenes and 1,2-dichloropropane in soil. Pestic. Sci. 7:325-335 (1976).
- Van Dijk, H. Degradation of 1,3-dichloropropenes in the soil. Agro-Ecosystems 1:193-204 (1974).